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A Zinc Phosphate Possessing Ladder-like Layers Made Up of Three- and Four-Membered Rings and Infinite Zn−O−Zn Chains

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A new open-framework zinc phosphate, $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$, possessing a layered architecture and consisting of alternating inorganic and organic layers, stabilized by multipoint hydrogen bonding has been synthesized hydrothermally. It has the following crystal data: monoclinic space group $C2/c$, $a = 25.075(5)$ Å, $b = 5.127(1)$ Å, $c = 17.726(4)$ Å, $\beta = 125.4(1)°$, $V = 1857.6(6)$ Å^3, $Z = 8$, $M = 748.3(1)$, $D_{calc} = 2.06$ g cm^{-3}, MoKα, and $R_F = 0.04$. The structure is made up of ZnO_4 and PO_4 tetrahedra linked though vertexes. The connectivity between the two units creates a layered structure with steps, the layers consisting of three- and four-membered rings only. This is the first instance of such a network in open-framework zinc phosphates. The exclusive presence of three-membered ring chains creates steps in the layers as well as an infinite number of Zn−O−Zn one-dimensional chains. Hydrogen bond interactions between the inorganic layers give rise to pseudo 10-membered ring channels, in which the diprotonated diethyelenetriamine molecules reside. The unusual T atom (T being Zn or P) connectivity in this material suggests the possibility of synthesizing many such materials with novel connectivities and networks.

Introduction

Open-framework metal phosphates and arsenates have been of interest because of their chemical and physical properties and the applications as catalysts, nonlinear optical materials, ion exchangers, etc.[1] The seminal work by Flanigen et al.[2] on aluminophosphates showed that phosphate frameworks can be made with zeolitic structures. Since the bivalent metal phosphates (+2 and +5) are associated with the same total charge as the aluminosilicate zeolites (+3 and +4), active research with phosphate-based framework materials containing divalent metals is being pursued. A large number of such zeolitic analogues have been isolated and characterized.[3,4] The framework structures of zeolites are generally built from tetrahedra-shared vertexes (usually Si and/or Al). This type of tetrahedral connectivity can be regarded mathematically as four-connected three-dimensional (3D) nets, constructed from three-connected two-dimensional (2D) sheets.[5] It so happens that four-connected 3D nets and three-connected 2D sheets are common among the open-framework structures. Bu et al.[6] have recently observed the layers that are constructed only by four-connected 2D sheets in a lamellar zinc arsenate. Though it is known that interruptions can occur within the layers disrupting the four-connected sheets,[7] with all the tetrahedral groups not making four bonding connections to their neighbors, there appear to be no examples of layered structures where the interruptions which occur within the layers create ladder-like steps. Such ladderanes are, however, observed in one-dimensional chains.[8] In this paper, we report, for the first time, a layered zinc phosphate structure wherein the layers form ladders as well as an infinite number of one-dimensional Zn−O−Zn chains. The unusual presence of chains exclusively formed by three-membered rings which border those containing four- or three- and four-membered rings in the layers is a unique feature of this material. Furthermore, the three- and four-membered rings show well-defined periodicity.

Experimental Section

Synthesis and Initial Characterization. The title compound, $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$, was synthesized under hydrothermal conditions using diethylenetriamine (DETA) as the structure-directing agent. In a typical synthesis, 0.2035 g of ZnO was dispersed in a mixture containing 0.288 mL of 85 wt % H_3PO_4, 0.15 mL of HCl, and 5.7 mL of water. To this solution was added 0.27 mL of diethylenetriamine (DETA), and the whole solution was stirred for 30 min. The final homogenized mixture was transferred

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Table 1. Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$

empirical formula	$Zn_4P_4O_{16}N_3C_4H_{17}$
crystal system	monoclinic
space group	$C2/c$
crystal size (mm^3)	$0.08 \times 0.14 \times 0.16$
a (Å)	25.075(5)
b (Å)	5.127(1)
c (Å)	17.726(4)
α	90.0
β	125.4(1)
γ	90.0
volume (Å^3)	1857.6(6)
Z	4
formula mass	748.28
ρ (g cm^{-3})	2.06
λ (MoKα) (Å)	0.71073
μ (mm^{-1})	4.16
temperature of measurement (K)	298
θ range (deg)	1.99−23.26
total data collected	3620
index ranges	$-27 \le h \le 25$, $-5 \le k \le 5$, $-16 \le l \le 19$
unique data	1334
observed data [$\sigma > 2\sigma(I)$]	1144
R_{int}	0.03
refinement method	full-matrix least-squares on $\lvert F^2 \rvert$
R indices [$\sigma > 2\sigma(I)$]	$R = 0.032$; $R_w = 0.08$
R (all data)	$R = 0.042$; $R_w = 0.084$
goodness of fit (S)	1.08
no. of variables	146
largest difference map peak and hole (e Å^{-3})	1.422 and −0.457

in a PTFE-lined stainless steel autoclave and heated at 180 °C for 128 h. The final composition of the mixture was ZnO:DETA:$2H_3PO_4$:2HCl:$125H_2O$. The resulting product predominantly contained large quantities of colorless rectangular plates. The crystals were filtered and washed thoroughly with deionized water. The initial characterization was carried out using powder X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Powder X-ray diffraction with powdered single crystals indicated that the products were new materials; the pattern is entirely consistent with that simulated from a single-crystal study. The TGA studies were carried out in static air in the range of 25−600 °C.

Single-Crystal Structure Determination. A suitable single crystal was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. Crystal structure determination by X-ray diffraction was performed on a Siemen's SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected at room temperature in 1321 frames with ω scans (a width of 0.30° and an exposure time of 20 s per frame). The final unit cell constants were determined by a least-squares fit of 2507 reflections in the θ range of 1.99−23.26°. The lattice parameters are as follows: $a = 25.075(5)$ Å, $b = 5.127(1)$ Å, $c = 17.726(4)$ Å, $\beta = 125.4(1)°$, $V = 1857.6(6)$ Å^3, space group $C2/c$, and $Z = 8$. A total of 3620 reflections were collected, and these were merged to give 1334 unique reflections ($R_{\text{merg}} = 0.03$), 1144 of which were considered to be observed when $I > 2\sigma(I)$. Pertinent experimental details for the structure determinations are presented in Table 1.

The structure was determined by direct methods using SHELXS-86[9] and difference Fourier syntheses. An absorption correction based on symmetry equivalent reflections was applied using SADABS[10]. Other effects, such as absorption by the glass fiber, were simultaneously corrected. All the hydrogen positions were initially located in the difference map, and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[11] package of programs. The final Fourier map had minimum and maximum peaks of −0.457 and 1.422 e Å^{-3}, respectively. Final R values for all the data ($R = 0.042$, $R_w = 0.084$, and $S = 1.08$) were obtained for a total of 146 parameters. The final atomic coordinates are given in Table 2.

Table 2. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [Å$^2 \times 10^3$] for $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$

atom	x/a	y/b	z/c	U(eq)[a]
Zn(1)	0.2048(1)	0.2860(1)	0.1826(1)	0.013(1)
Zn(2)	0.0751(1)	0.7083(1)	0.0506(1)	0.016(1)
P(1)	0.2164(1)	0.7850(3)	0.0989(1)	0.012(1)
P(2)	−0.0671(1)	0.7724(3)	−0.1435(1)	0.014(1)
O(1)	0.1133(2)	0.3697(7)	0.1231(2)	0.018(1)
O(2)	0.2370(2)	0.5020(7)	0.1272(3)	0.018(1)
O(3)	0.2427(2)	−0.0563(7)	0.1902(2)	0.017(1)
O(4)	0.0007(2)	0.6616(9)	−0.0740(3)	0.032(1)
O(5)	0.0716(2)	0.9359(7)	0.1340(3)	0.030(1)
O(6)	0.1427(2)	0.8206(8)	0.0352(3)	0.022(1)
O(7)	−0.0884(2)	0.7102(8)	−0.2410(3)	0.027(1)
O(8)	0.2486(2)	0.8972(7)	0.0545(2)	0.018(1)
N(1)	−0.1449(2)	0.2412(10)	−0.3371(4)	0.031(1)
N(2)	0.0000	0.4082(15)	−0.2500	0.041(2)
C(1)	−0.1119(3)	0.2764(19)	−0.3848(5)	0.075(3)
C(2)	−0.0395(3)	0.2170(18)	−0.3273(6)	0.099(4)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

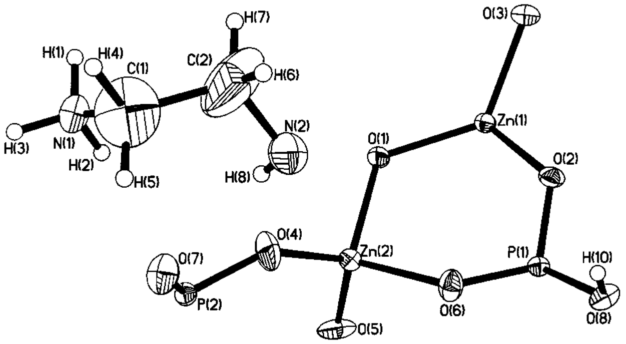

Figure 1. Ortep plot of $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$ showing the labeling scheme. Thermal ellipsoids are shown at 50% probability.

Results and Discussion

The asymmetric unit of the zinc phosphate, $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$, being studied contains 16 independent non-hydrogen atoms, 12 of which belong to the "framework" (two Zn, two P, and eight O atoms) and four to the guest (two N and two C atoms) (Figure 1 and Table 2). Of the eight oxygens in the asymmetric unit, two are three-coordinated linking two Zn atoms and one P atom (25%) and the remaining

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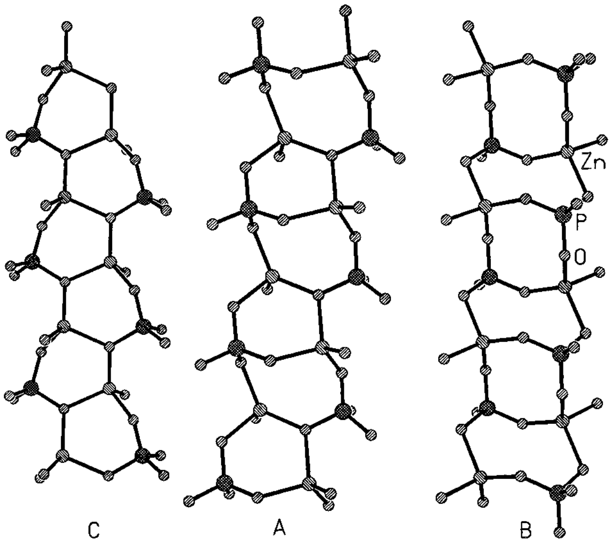

Figure 2. Figure showing the different type of chain arrangements that are seen in $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)\ ]^-$.

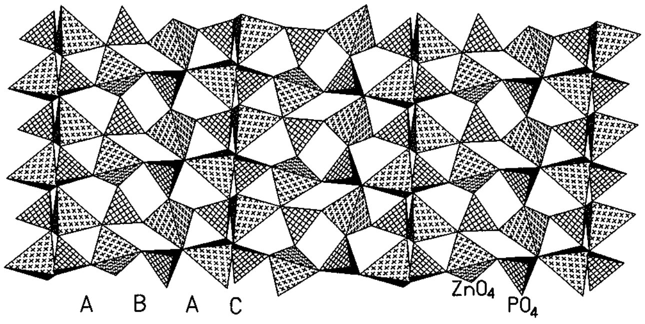

Figure 3. Polyhedral view of $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$ along the [010] direction showing the layers, the various chains, and the connectivity between them. Note that the three-membered ring (C type) forms the step in the layer.

six are normal Zn−O−P links. The linkages involving the three-coordinated oxygen atoms result in the formation of three-membered rings in this material.

The framework structure is made from the tetrahedral linkage between ZnO_4 and PO_4 moieties sharing the vertexes. The connectivity between these units forms layers, which are anionic. The structure-directing agent, ditheylenetriamine (DETA), is doubly protonated and occupies spaces between the layers. Thus, the entire structure can be considered to be made up of alternating anionic (inorganic) and cationic (organic) layers. The connectivity between the ZnO_4 and PO_4 units is such that it produces three distinct types of chains, labeled A−C in Figure 2. The A type chain consists of alternate stacks of three- and four-membered rings [involving Zn(1) and Zn(2)], while the B type chain is made up of only four-membered rings [involving only Zn(2) and P(2)]. The C type chain is made up of only three-membered rings [involving only Zn(1) and P(1)] (Figure 2). The chains are connected to one another other forming the layer as shown in Figure 3. To our knowledge, this zinc phosphate is the first example of an open-framework material where different types of chain arrangements are connected to each other forming a layer with ladder-like steps. Isolated and short chain three-membered rings are common in many of the open-framework zinc phosphates,[12−15] but this is the first instance of a continuous three-membered ladder (chain) being present in an open-framework material. The presence of the exclusive three-membered chains of ladders creates some strain in the layer, which is otherwise nearly planar and causes the formation of a step and a ladder-like feature in the material. Furthermore, we find an ABAC repeating unit along the *bc* plane giving rise to the repeat ring sequence of 3343344433 along the *c* axis (Figure 3). When it is recalled that the three-membered ring is the smallest possible ring size and that two three-membered rings can make a four-member ring, the present structure can, in principle, evolve into a layer structure with only four-membered rings which are rarely seen in open-framework materials.

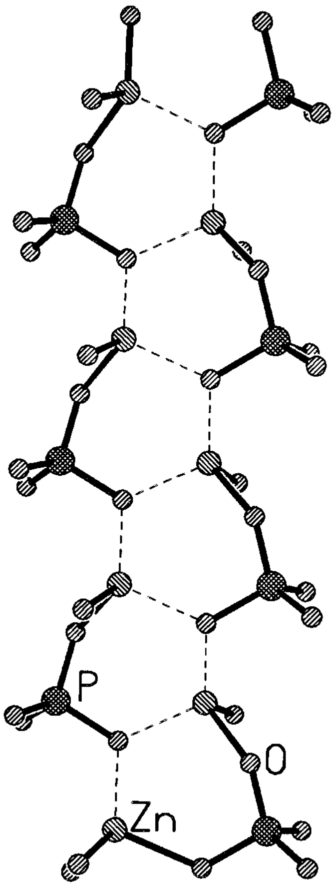

Figure 4. Structure showing the infinite number of one-dimensional Zn−O−Zn chains (dashed lines), formed due to the presence of three-membered ladders, observed in $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$.

The framework of the zinc phosphate examined here is also characterized by the presence of an infinite number of Zn−O−Zn chains (Figure 4). The Zn−O−Zn linkage is accompanied by the trigonal coordination of the bridging oxygen atoms, the third coordination being always to a P atom. Such a trigonal coordination of the oxygen atom in the Zn−O−Zn bridge is an electrostatic

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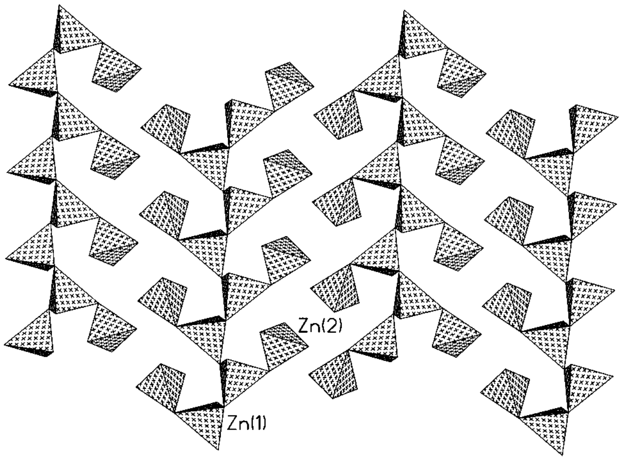

Figure 5. Zn tetrahedra subnetwork showing the fish backbone arrangement.

valence requirement of the bridging oxygen atoms. Twenty-five percent of the oxygens in the asymmetric unit are three-coordinated (two of the eight framework oxygen atoms). Thus, it cannot be concluded that the presence of three-coordinated oxygen bridges tends to give rise to more dense frameworks. There are other examples of such electrostatic valence requirements of oxygens that have been identified in the literature.[12−15] The trigonal and tetrahedal coordination of the oxygen atoms observed in some of the structures reported in the literature[12−15] suggests that these bridges occur when divalent tetrahedral atoms are involved. It is therefore to be expected that the presence of such features in the zinc phosphate system would lead to novel open-framework topologies which have no structural counterparts in aluminosilicates or aluminophosphates. The infinite one-dimensional Zn−O−Zn chain is formed only by the Zn(1) atoms (forming the three-membered ladders) as shown in Figure 4, but isolated short chain Zn−O−Zn linkages involving both Zn(1) and Zn(2) atoms are also present in this structure.

An interesting aspect of this layered zinc phosphate is the connectivity between the Zn atoms within each layer. From the Zn subnetwork shown in Figure 5, it can be seen that the arrangement resembles the fish backbone. This feature has been seen for the first time in this study. The Zn(1) forms the vertebrae onto which Zn(2) atoms are grafted completing the fish backbone type arrangement. This type of connectivity may be attributed to the presence of the three-membered chains and the three-coordinated oxygen atoms.

The connectivity between the ZnO_4 and PO_4 units gives rise to another unique feature whereby each Zn atom is surrounded by three- and four-membered rings. The circuit symbol, which enumerates the six distinct, smallest T atom loop pathways[5] (including the central atom itself), can be written as 4^46^2 or [4,4,4,4,6,6] for all tetrahedral atoms. This type of tetrahedral atom configuration has not been identified in aluminosilicates or aluminophosphates. In this material, Zn(1) and Zn(2) are connected to P through all four vertexes of the tetrahedron, whereas P(1) and P(2) are connected to Zn atoms only through three vertexes, the remaining vertice being a terminal oxygen (Figure 6). Thus, 50% of the T atoms are four-connected. There is, however, one example of a zinc arsenate where all the T atoms are four-connected.[6]

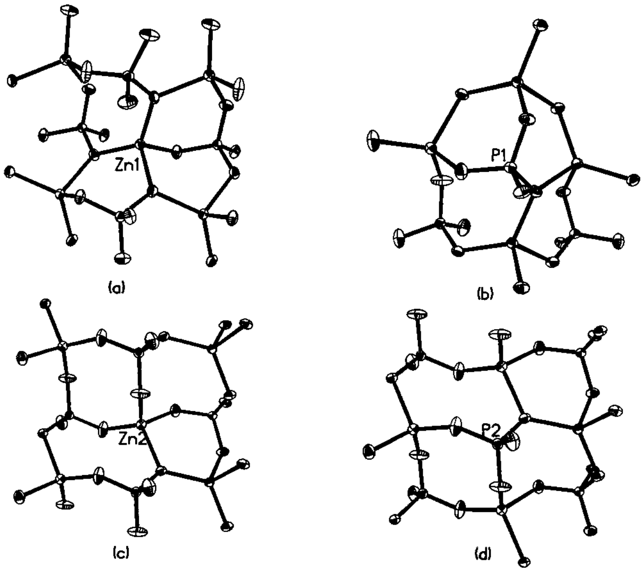

Figure 6. Detail of the environment around Zn(1), P(1), Zn(2), and P(2). Note that the $Zn(1)O_4$ unit is bonded to an eight-membered ring of neighboring TO_4 groups and the $P(1)O_4$ unit is bonded to a six-membered ring of neighboring TO_4 groups (see the text).

The Zn(1) atom is surrounded by three three-membered rings and one four-membered ring and makes four-membered and five-membered loops; the Zn(2) atom is surrounded by a three-membered ring and three four-membered rings and makes five-membered and six-membered loops (Figure 6a−d). The T atom connectivity observed in this material can be represented in the circuit symbol of Smith[5] as [3,3,3,4,4,5] and [3,4,4,4,5,6]. Although the loop configurations for Zn(1) and Zn(2) are different, it is to be noted that both of them are bonded into an eight-membered ring of neighboring TO_4 groups. The loop configuration for P(1), though identical to that of Zn(1), however, is bonded into a six-membered ring of neighboring TO_4 groups (Figure 6a,b). P(2), on the other hand, is identical to Zn(2) bonded into an eight-membered ring of neighboring TO_4 groups. We believe that this is the first time such a loop network for a T atom has been observed in an open-framework material.

The coordination environment of the various sites in this material can also be represented using the Schläfli symbol which specifies the connectivities of the various vertex-linked polygons. The description of the various types of plane nets, commonly observed in crystal chemistry, using the above symbolism has been reviewed by O'Keeffe and Hyde.[16] Acccording to the Schläfli notation, the coordination environment for P(1) can be represented as $\mathbf{3}^3\mathbf{4}^1$, meaning P(1) is surrounded by three triangles (three-membered rings) and one square (four-membered rings). Likewise, the notation for the other species would be as follows: P(2), $\mathbf{3}^1\mathbf{4}^3$; Zn(1), $\mathbf{3}^6\mathbf{4}^1$; and Zn(2), $\mathbf{3}^2\mathbf{4}^3$. This type of representation clearly shows the different situation for each site and its connectivity (Figure 6a−d).

The layered structure of the framework is stabilized by hydrogen bonding between the P(1)−O(8)H and that

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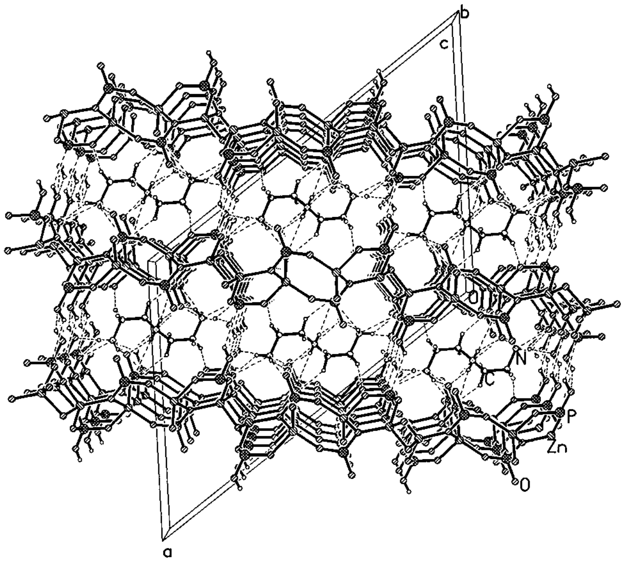

Figure 7. Structure of $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$ along the [001] direction showing alternating anionic and cationic layers and pseudo 10-membered channels. The amine molecule sits in the middle of the channels.

of the next layer leading to the formation of a pseudo 10-membered channels (Figure 7). Unlike in aluminosilicates,[17] the 10-membered ring is rare in open-framework zinc phosphate materials, having been identified only in one material so far.[18] The formation of such pseudo channels by hydrogen bonding between the terminal PO_4 and $PO_3(OH)$ of adjacent layers is known to occur in layered zinc phosphates.[19] The guest molecule, diethylenetriamine, is doubly protonated and occupies the interlamellar space formed by the framework species and sits in the middle of the pseudo 10-membered channels (Figure 7). The DETA molecule also participates in strong hydrogen bonding with the framework which lends additional structural stability to this material. The selected hydrogen bond interactions that are observed are presented in Table 4.

The ZnO_4 tetrahedra have Zn−O distances in the range of 1.908−2.039 Å [1.962 Å for Zn(1) and 1.956 Å for Zn(2)]. The O−Zn−O bond angles are in the range of 98.4−127.5° [average of 108.8° for Zn(1) and 109.2° for Zn(2)]. The tetrahedral P atoms have P−O bond distances in the range of 1.516−1.580 Å [average of 1.537 Å for P(1) and 1.532 Å for P(2)] and O−P−O bond angles in the range of 105.5−113.5° [average of 109.5° for P(1) and 109.5° for P(2)]. The longest bond distances and the largest bond angles, however, are observed for oxygens involved in three-coordinated systems. One of the P−O distance [P(1)−O(8)] is protonated leading to the formation of HPO_4 units in the material. These values are typical of Zn and P in a tetrahedral oxygen environment. From the above values, it is clear that the P atoms form more regular tetrahedrons than the Zn atoms. The selected bond distances and angles are presented in Table 3.

Table 3. Selected Bond Lengths and Angles for $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$

moiety	distance (Å)	moiety	distance (Å)
Zn(1)−O(1)	1.938(4)	P(1)−O(2)	1.524(4)
Zn(1)−O(2)	1.939(4)	P(1)−O(6)	1.518(4)
Zn(1)−O(3)	1.962(4)	P(1)−O(8)	1.529(4)
Zn(1)−O(3)^1	2.008(3)	P(1)−O(3)^2	1.574(4)
Zn(2)−O(1)	2.039(4)	P(2)−O(4)	1.516(4)
Zn(2)−O(4)	1.908(4)	P(2)−O(7)	1.517(4)
Zn(2)−O(5)	1.925(4)	P(2)−O(5)^3	1.517(4)
Zn(2)−O(6)	1.953(4)	P(2)−O(1)^4	1.580(4)

moiety	angle (deg)	moiety	angle (deg)
O(1)−Zn(1)−O(2)	107.8(2)	O(6)−P(1)−O(2)	113.2(2)
O(1)−Zn(1)−O(3)	127.5(2)	O(6)−P(1)−O(8)	110.5(2)
O(2)−Zn(1)−O(3)	102.6(2)	O(2)−P(1)−O(8)	110.4(2)
O(1)−Zn(1)−O(3)^1	108.7(2)	O(6)−P(1)−O(3)^2	107.9(2)
O(2)−Zn(1)−O(3)^1	98.4(2)	O(2)−P(1)−O(3)^2	107.1(2)
O(3)−Zn(1)−O(3)^1	107.91(10)	O(8)−P(1)−O(3)^2	107.6(2)
O(4)−Zn(2)−O(5)	121.0(2)	O(4)−P(2)−O(7)	109.7(2)
O(4)−Zn(2)−O(6)	102.8(2)	O(4)−P(2)−O(5)^3	113.6(3)
O(5)−Zn(2)−O(6)	111.0(2)	O(7)−P(2)−O(5)^3	109.5(2)
O(4)−Zn(2)−O(1)	114.2(2)	O(4)−P(2)−O(1)^4	105.5(2)
O(5)−Zn(2)−O(1)	104.3(2)	O(7)−P(2)−O(1)^4	110.0(2)
O(6)−Zn(2)−O(1)	102.1(2)	O(5)^3−P(2)−O(1)^4	108.4(2)

moiety	angle (deg)	moiety	angle (deg)
P(2)^4−O(1)−Zn(1)	124.6(2)	P(2)^4−O(1)−Zn(2)	113.0.4(2)
P(1)−O(2)−Zn(1)	123.3(2)	Zn(1)−O(1)−Zn(2)	120.5(2)
P(1)^5−O(3)−Zn(1)	119.6(2)	P(2)−O(4)−Zn(2)	141.0(3)
P(1)^5−O(3)−Zn(1)^6	123.9(2)	P(2)^3−O(5)−Zn(2)	136.3(3)
Zn(1)−O(3)−Zn(1)^6	114.4(2)	P(1)−O(6)−Zn(2)	129.9(2)

Organic Moiety

moiety	distance (Å)	moiety	angle (deg)
N(1)−C(1)	1.4994(11)	C(2)−N(2)−C(2)^7	98.3(10)
N(2)−C(2)	1.4992(11)	N(1)−C(1)−C(2)	115.8(6)
N(2)−C(2)^7	1.4993(11)		
C(1)−C(2)	1.5090(12)		

Table 4. Selected Hydrogen Bond Interactions in $[NH_3(CH_2)_2NH(CH_2)_2NH_3]^{2+}2[Zn_2PO_4(HPO_4)]^-$

moiety	distance (Å)	moiety	angle (deg)
O(7)−H(1)	2.246(1)	O(7)−H(1)−N(1)	157.03(9)
O(7)−H(2)	2.042(1)	O(7)−H(2)−N(1)	143.7(1)
O(8)−H(3)	2.131(1)	O(8)−H(3)−N(1)	141.7(1)
O(7)−H(8)	2.164(1)	O(7)−H(8)−N(2)	147.1(1)
O(8)−H(10)^a	1.760(1)	O(8)−H(10)−O(8)^a	146.2(1)
O(6)−H(4)	2.371(1)	O(6)−H(4)−C(1)	156.4(1)
O(5)−H(6)	2.530(1)	O(5)−H(6)−C(2)	139.4(1)

[a] Interaction between two framework layers.

Thermogravimetric analysis (TGA) carried out in static air indicates only one sharp mass loss in the region of 240−260 °C. The mass loss of 25% corresponds to the loss of amine from the structure (calculated value of 24.2%) and subsequent collapse of the framework. The decomposed sample was found to be poorly crystalline (powder XRD) and corresponds to a dense zinc phosphate, indicating the loss of framework structure with the loss of the amine.

Conclusions

The synthesis and structure of a new layered zinc phosphate, containing alternating iroganic and organic layers, formed by three- and four-membered rings possessing ladder-like layers and an infinite number of Zn−O−Zn chains has been accomplished. The guest molecule, doubly protonated diethylenetriamine, oc-

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cupies spaces between the inorganic layers and interacts with the anionic framework through hydrogen bonding. Unlike in aluminosilicates, where the framework charge can be matched with that of the templates by increasing the Si:Al ratio with only a small change in the framework topology, a change in the Zn:P ratio generally leads to completely different frameworks. Thus, in the zinc phosphates, we have a limited ability to vary the framework charge distribution to match that of the template, without significantly altering the framework structure. The observation of a new type of T atom connectivity in the title compound indicates that it is worthwhile to explore this area further as many new materials with novel structural features may be discovered.

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